ADSORPTION OF Pb(II) ON DURIAN LEAVES

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Abstract

In order to reveal the performance of Durian Leaves (DL) as a putatively advantageous biosorbent for the removal of Pb(II) from aqueous solution, the kinetic of biosorption, and the physio-chemical factors on biosorption were investigated comprehensively. DL was characterized by using pHslurry and pHpzc of biosorbent. The effect of physicochemical such as pH, adsorbent dosage, initial concentration of Pb(II) and contact time has been studied to obtain the optimum condition to remove Pb(II) ion from the aqueous solution. The studies were conducted at pH 4, DL dosage 0.04 g, and in contact time of 90 minutes. Kinetic data were analyzed by using two adsorption kinetic models which are pseudo-first-order and pseudo-second-order. The data shows high correlation coefficient based on pseudo-second-order model with R^2 is 0.9905 rather than pseudo-first-order model. Our results demonstrate that the DL is a promising biomass-based biosorbent for the removal of Pb(II) from wastewater for its fine capacity of biosorption.

Keyword: Biosorption, Durian leaves, Kinetics, Pb(II)

Introduction

Surface water quality degradation is caused by human activities through industrial and agricultural processes. This problem leads to the poor quality of water supply or lack of recycled wastewater. Lead water pollution is one of the main environmental problems because heavy metals are non-biodegradable and harmful to public health. The high contaminant level of lead is very dangerous due to its toxicity. Lead is a chemical element that can be found everywhere and mostly resulted from human activities such as manufacturing, burning fossil fuels and mining. Lead can enter the ecosystem in the form of atmospheric lead, ammunition, paint chips, pesticides, lead acid batteries and other industrial products.

A variety of methods can be applied to minimize lead concentration in wastewater which involve chemical precipitation, electrolytic reduction, membrane technology, adsorption and ion exchange (Vijayaraghavan & Balasubramanian, 2015). However, most of these methods have some disadvantages such as high operation cost and ineffective when used at higher concentration (Hafshejani et al., 2015). Regardless, the adsorption method can be used to remove contaminants especially lead. Adsorption can ensure treatment stability, decreasing environment impact, lower the cost and easy to handle the operation (Hafshejani et al., 2015).

There are various adsorbents to remove lead from water and wastewater that have been investigated and researched on with results showing that using adsorbent from plant waste give various advantages for wastewater treatment including good adsorption capacity, simple method, lower cost and ease of regeneration (Wan Ngah et al., 2013). Significantly, this study can give a new pace in studying natural adsorbent like Durian leaves for future research in removing heavy metals. Durian (*Durio zibethinus Murray*) is one of the tropical fruits rich with nutrients and high in bioactive properties. By nature, durian is locally known as the king of

fruits and the second biggest produce in Malaysia. The development of durian has been sensational in the worldwide exchange of the business sector. The waste from durian such as leaves, bark, durian rind and seed are being discarded as solid waste.

The main objective of this study is to investigate the adsorption performance of lead from aqueous solution by using durian leaves powder (DLP). The influences of physicochemical parameters such as pH_{slurry}, pH_{pzc}, adsorbent dosage, initial lead concentration and contact time on lead adsorption process are investigated in batch mode studies. In addition, the evaluation of kinetic adsorption is determined by pseudo-first-order model and pseudo-second order model. To our best knowledge, this study has not been reported so far.

Materials and Methods

Sample collection

The durian leaves (DL) were washed with tap water to remove any dust and soluble impurities. At 105 ˚C in the oven, the DL were dried overnight before they were sieved and ground to get a constant particle size of 120-250 µm. A glass bottle was used to store the durian leaves powder (DLP) for further analysis.

Reagents

All chemicals used were of analytical grade. Stock solution of 1 g/L Pb(II) was prepared from $Pb(NO_3)_2$ dissolution in deionized water. The working solutions were obtained by diluting the stock solution in deionized water.

Adsorbent characterization

pH aqueous slurry (pHslurry)

0.1 g of DLP was dissolved in 100 mL deionized water. The sample was stirred at 120 rpm for 24 hours. The measurement of pH was tested by using pH meter. pH slurry was determined to identify whether the adsorbent was acidic or basic.

pH zero point charge (pHpzc)

25 mL of 0.01 M KNO_3 was prepared with the initial range between pH 2 to 9 into different conical flask. The formation of specific pH was adjusted using 0.1 M HCl and 0.1 M NaOH. 0.1 g of the DLP was added into each conical flask and the solution was stirred overnight at room temperature. The solution was filtered and the final pH was measured. The graph of pH versus ΔpH was plotted in order to determine the pHpzc.

Batch sorption experiment

The batch mode of experiment was performed by using 0.02 g of DLP and 50 mL of Pb(II) test solutions, under thermostated water bath shaker with 120 stroke/min and at room temperature. The influence of the initial pH of the solution was studied within the range of 2–12 at room temperature and a contact time of 180 minutes. The initial pH was adjusted to 0.1 M NaOH or 0.1 M HCl. The initial and final pH of the solution were measured with the pH meter. The effect of adsorbent dosage was done by varying the mass range of 0.02 to 1.0 g of DLP. Kinetics measurements were done at three initial concentrations (20 and 30 mg/L) and aliquots were taken at different time intervals (10 to 120 minutes) to determine the Pb(II) concentration. The pH of the mixture was adjusted to reach the optimum pH. The metal solution was separated from the sorbent by filtrations and was analyzed by using Atomic Adsorption Spectrophotometer (AAS) at the maximum wavelength (λ max) of Pb(II). All tests were realized in duplicate and the average values were reported. The amount of metal ion retained

at equilibrium (qe) and the Pb(II) removal efficiency (R) were calculated with the following equations:

$$q_e = \frac{C_O - C_e}{m} V \quad (1)$$

$$Removal\ (\%) = \frac{C_O - C_e}{C_O} x100 \quad (2)$$

where C_0 and C_e are initial and final Pb(II) concentrations after adsorption process respectively (mg L^{-1}), V is the volume of MB solution (L), and m is the mass of adsorbent (g).

Results and Discussion

Adsorption characterization

Biosorbent surface performance and metal speciation are affected by the pH of the solution (Irina et al., 2017). From the pH analysis of the adsorbent, the value of pH DLP is at 6.98 which indicated that DLP is a neutral adsorbent. The pH at zero point charge, pH_{pzc} was analysed to observe the type of charge on the surface of DLP. The determination pH_{pzc} was important to biosorption mechanism and the properties of an adsorbent surface. There is a relationship between pH_{zpc} and $pH_{slurry.}$ When pH_{slurry} is higher than pH_{zpc}, the surface becomes negatively charged and has the tendency to attach Pb(II) ion in solution to the ion surface. However, when pH_{slurry} is lower than pH_{zpc}, the surface becomes positively charged in which electrostatic repulsion occurs with Pb(II) ion and the adsorption rate of Pb(II) ion becomes low (Reddy et al.,2010). **Figure 1** shows the variation $\Delta pH=pHi-pH_f$ vs. the initial pH, pH_i for DLP.

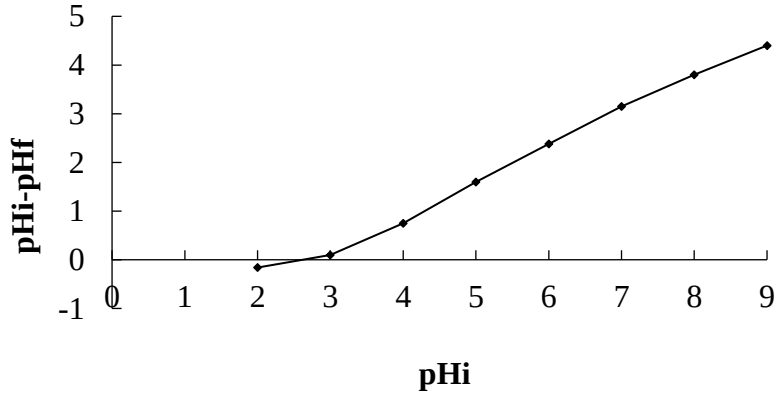

Figure 1 The variation $\Delta pH=pHi-pH_f$ vs.the initial pH, pH_i during Pb(II) adsorption on DLP

The pH_{pzc} is identified as the pH at which ΔpH is zero. Based on Figure 1, pH_{pzc} for DLP that has been observed is 2.5. The pH_{pzc} shows that DLP have the ability to adsorb Pb(II) due to the negatively surface charged.

Effect of pH

Analysis of variable pH solution is an important parameter in the adsorption process to determine the optimum pH for maximum Pb(II) ion removal (Anwar et al., 2010). This is because pH is used to determine the ionic state of functional groups on adsorbent surface and also affects the chemical speciation of heavy metals in solution (Fadzil et al., 2016). The result of pH values versus Pb(II) adsorption capacity (qe) in this study, is shown in **Figure 2**.

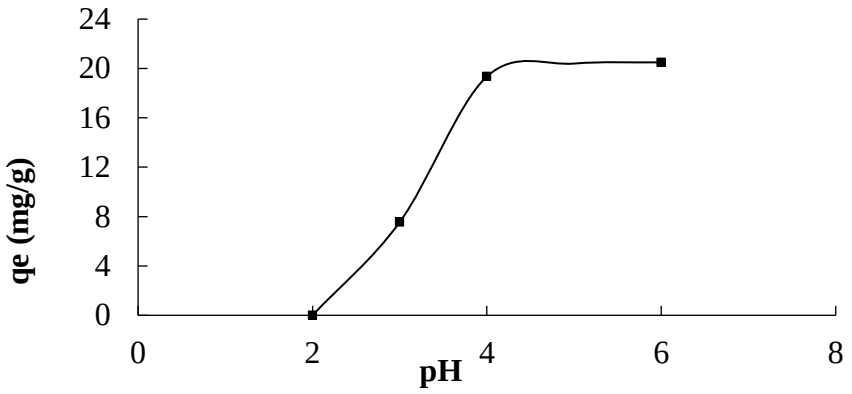

Figure 2 Effect of pH on Pb(II) ion adsorption on DLP

It was observed that the values of adsorption capacity of Pb(II) on DLP was increased from pH range of 2.0 to 6.0. The presence of active site on adsorbent surface was affected by the competition between hydrogen ions and Pb(II) at the different pH values. At values of pH lower than pH_{PZC} the surface of DLP is positive and the biosorption of Pb(II) ions are positively charge. Consequently, the metal ions from the solution could replace the H^+ of the active centers of the sorbent. This could be the reason for the small change in the final solution pH. However, as the pH increases and the pH is higher than pH_{PZC}, the electrostatic repulsion decreases due to the reduction of the positive charge density of protons on the sorption sites, thus resulting in an enhancement of Pb(II) biosorption. Even though the results was showed that the higher uptake capacity is at pH 5, but pH 4 was chosen for further analysis due to its higher stability of Pb(II) ion.

Effect of adsorbent dosage

Figure 3 shows the uptake capacity of Pb(II) ion that evaluates the relationship between DLP dosage and Pb(II) adsorption. Adsorbent dosage is an important role that determines how much adsorbent is needed to remove metal ions from the solution. The adsorption capacity (qe) of the Pb((II) ions was decreased with the adsorbent dosage from 0.02 g/L to 0.1 g/L. This happened due to the decrease of available contact area and lead binding efficiencies of DLP (Noor et al., 2017). Therefore, an optimum adsorbent dosage for Pb(II) adsorption was selected at 0.04 g for further analysis. Large amount of adsorbent in the solution will affect the adsorbent particles which tend to form larger particles. Thus, their surface area and the adsorption potential would be decreased.

Effect of initial concentration and contact time

The study on the initial concentration and contact time on the adsorption studies was an important parameter in the water and wastewater treatment system (Hafshejani et al., 2015). This was determined by using different concentration 20 and 30 mg/L of Pb(II) standard solution with different range of time between 10 to 120 minutes. **Figure 4** shows the relationship between the initial concentration and contact time of DLP

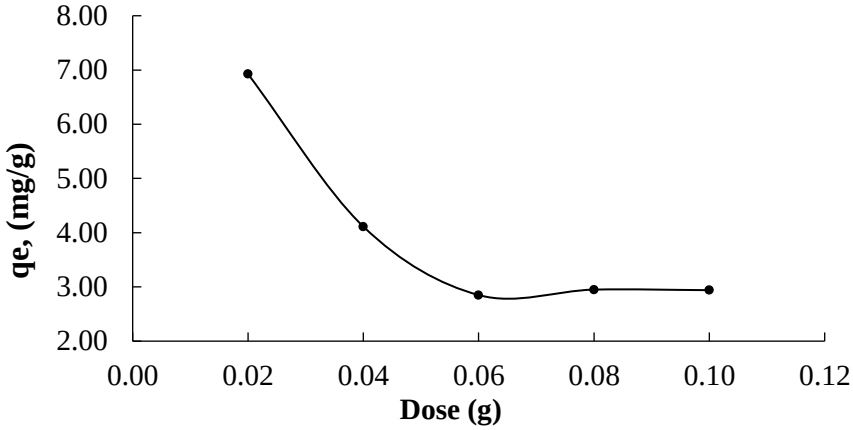

Figure 3 Effect on DLP dosage on Pb(II) adsorption onto DLP

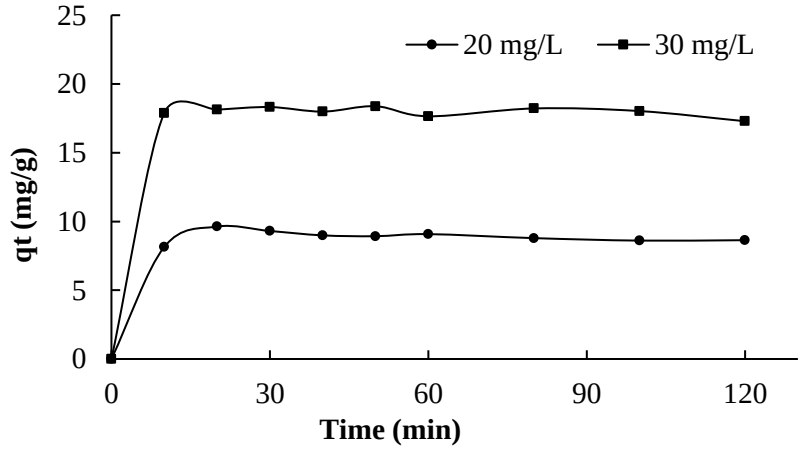

Figure 4 Effect of initial concentration and contact time of DLP

The trend in **Figure 4** showed that the three main phases were involved during the reaction. The rate of the adsorption was classified to three phases which were slow phases, medium phases or dynamic equlibrium phases and fast phases. At the first 10 minutes, the adsorption rate was very fast. However, the rate of adsorption reduced after 60 minutes reaction time. Many adsorption site was exposed for adsorption during the beginning phases and after 60 minutes, the remaining surface sites were decreased (Abdessalem et al., 2016). The equilibrium time of 90 minutes was selected for further analysis. Adsorption capacity for 30 mg/L is higher than 20 mg/L due to larger amount of Pb (II) molecules adsorbed which caused by faster driving force to overcome the mass transfer resistance to the surface of DLP (Fouzi et al., 2018).

Kinetic studies

Adsorption process is time dependent, so it is very important to know the rate of the adsorption process. Furthermore, the kinetics was deal with changes in chemical properties over the time and dependent with the rate of changes (Azizan, 2004). In regards to this study, the adsorption kinetics was analysed by using two common models, pseudo-first-order and pseudo-second-order models.

Pseudo-first-order model has been proposed by Lagergren (1898) for adsorption analysis to describe the sorption of liquid on solid. The non linear equation and the reversibility of the equilibrium between liquid and solid phases were described in this model. The linearized

equation of the pseudo-first-order was used in this study is expressed in the following equation 3:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

where q_e (mg/g) and q_t (mg/g) is the amount of Pb(II) adsorbed on the adsorbent at time t and $k_1(min^{-1})$ is the rate constant of first-order adsorption process, q_e is the equilibrium sorption uptake which is extrapolated from the experimental data at time t = infinity. k_1 value is equal to the slope of the plotted graph as in **Figure 5** linear plots of log (q_e- q_t), versus t was used to evaluate the data.

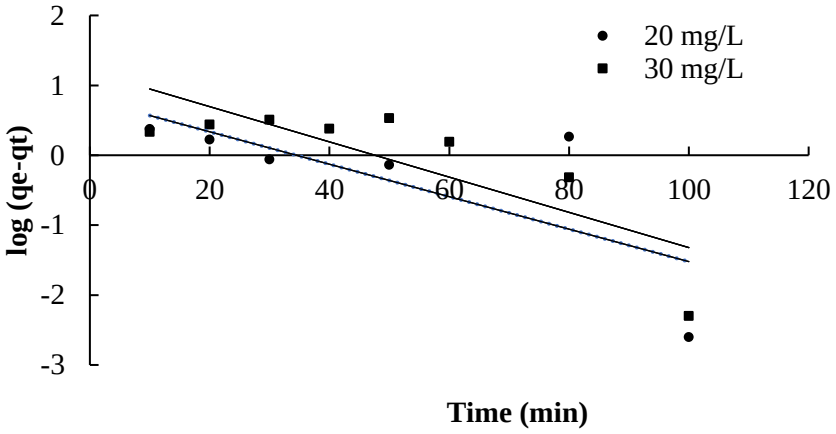

Figure 5 Pseudo-first-order plot on Pb(II) adsorption onto DLP

All the data which include calculated and experimental q_e values, pseudo-first-order rate constant and correlation coefficient (R^2) were tabulated in Table 1. Values of k_1 for the pseudo-first-order kinetic model were obtained from the slopes of the linear plots of log(q_e- q_t) versus t for all concentrations. Since the R^2 value of pseudo-first-order was far from 0.999-1, so the biosorption process did not fit with this kinetic model. The lowering of the R^2 values showed that the experimental q_e value deviated far from the calculated q_e.

The pseudo-second-order kinetic model indicated that the rate of limiting step might be due to the chemical adsorption or chemisorption (Fadzil et al., 2016). The linearized form of pseudo-second-order equation is as in equation 4:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (4)$$

While h is equal to $k_2 {q_e}^2$ and k_2(g/mg min) is the rate constant of the adsorption, q_e (mg/g) is the amount of metal adsorbed at equilibrium, q_t (mg/g) is the amount of metal adsorbed at times. The values of the calculated and experimental q_e are represented in Table 1. The plot of t/qt versus t was plotted to evaluate q_e and k_2 values that appered from the slopes and intercepted of the plot in the **Figure 6**.

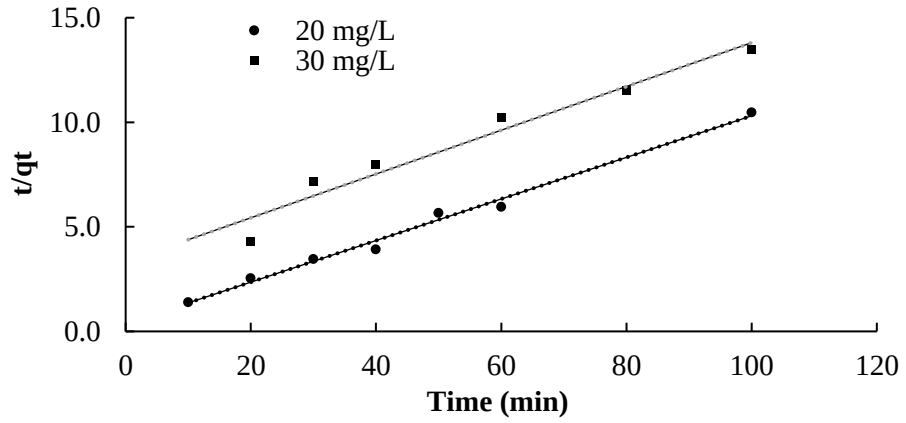

Figure 6 Pseudo-second-order plot on Pb(II) adsorption onto DLP

Table 1 shows that the correlation coefficient, R^2 from both kinetic models were deemed more agreeable for pseudo-second-order compared to pseudo-first-order. Hence, it can be concluded that the pseudo-second-order is chemisorption in which the rate of limiting step involves sharing or exchange of electrons between sorbent and sorbate (Fadzil et al., 2016).

Table 1 Pseudo-first-order and pseudo-second-order parameter at various Pb(II) concentration on DLP

[Pb] mg/L	q_e, exp (mg/g)	Pseudo-First-Order			Pseudo-Second-Order		
		q_e, cal (mg/g)	k_1 (min^{-1})	R^2	q_e, cal (mg/g)	k_2 (min^{-1})	R^2
20	17.28	6.31	0.058	0.527	9.55	0.031	0.955
30	27.29	15.83	0.053	0.642	10.06	0.257	0.991

Conclusion

Based on equilibrium studies, Pb(II) ions adsorption are strongly influenced by contact time, initial concentration, pH and adsorbent dosage. The optimum condition for Pb(II) adsorption on Durian Leaves Powder (DLP) was attained at pH 4, the DLP dosage of 0.04 g and in the contact time of 90 minutes. The kinetic models for adsorption of Pb(II) on the DLP showed that the pseudo-second order model is closer to 1 compared to the pseudo-first-order. Thus, the pseudo-second-order was suitable to explain the kinetics of adsorption for this study. Further extended research include more additional operating parameters for adsorption process, sorbent regeneration and physical characterization studies.

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Conflict of interests

Author hereby declares that there is no conflict of interests with any organization or financial body for supporting this research.

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